DESCRIPTION

PARTICULATE MATTER OXIDATION CATALYST AND FILTER

5   Technical Field

This invention relates to a catalyst used for the combustion of particulate matter (PM) contained in the exhaust gas of diesel engines, and to a particulate matter filter for control of diesel engine exhaust emissions using this catalyst.

10   Background Art

Nitrogen oxides (NO_x) and particulate matter (PM) are particular problems with respect to diesel engine exhaust. Among these, the particulate matter comprises fine particles constituted primarily of carbon, and the most typical method of their removal has been a method whereby a diesel particulate filter (DPF) is placed in the exhaust line to trap

15   the particulate matter. The trapped particulate matter is burned intermittently or continuously, thus regenerating the particulate filter.

This filter regeneration process may be performed by a method wherein an electric heater, burner or the like is used to burn the particulate matter, or a method wherein the particulate filter carries a catalyst, and its catalytic effect lowers the ignition

20   temperature of the particulate matter, thereby continuously burning the particulate matter at the exhaust gas temperature. The former method requires the addition of outside energy and the system becomes complex, so the latter catalytic method is considered to be preferable.

Examples of this catalytic method include those disclosed in Patent Reference Documents 1 and 2 and Non-Patent Reference Documents 1 and 2, where

25   platinum (Pt) is used as the catalyst metal. However, a way of solving the problem of

increased costs due to the use of noble metals as the catalyst is an important problem.

Patent Reference Document 3 recites the use of a perovskite-type composite oxide in a DPF, and indicates that the carbon black ignition temperature is decreased by the use thereof.

5   Non-Patent Reference Document 3 proposes the use of V_2O_5, MoO_3, PbO, Cs_2MoO_4, $AgVO_3$ or eutectic mixtures thereof as melt moving type catalysts. These mixtures melt at exhaust gas temperatures, move over the surface of a honeycomb substrate, come into contact with particulate matter and oxidize and burn it. Thus, the lower the melting point and higher the mobility of the mixtures, the greater the effect of burning

10   particulate matter at low temperature becomes, so these are said to be more superior as catalysts. However, such low-melting point substances are highly volatile, so they have a problem in that their durability is low. Consequently, they have yet to find practical application.

Non-Patent Reference Document 4 proposes the use of a perovskite-type

15   composite oxide containing potassium (K). However it is difficult for K to be completely contained within the structure of a perovskite-type composite oxide, and thus the K that could not be incorporated into the structure is present in oxide or hydroxide form, so it is readily eluted into moisture within the exhaust gas, again posing a problem of durability.

Patent Reference Document 1: JP Hei 11-253757 A

20   Patent Reference Document 2: JP 2003-222014 A

Patent Reference Document 3: JP Hei 06-29542 B

Non-Patent Reference Document 1: *Earozoru Kenkyū* ["Aerosol Research," published by the Japan Association of Aerosol Science and Technology] (2003), Vol.18, No. 3, pp. 185–194

25   Non-Patent Reference Document 2: *Jidōsha Gijutsu Kai Gakujutsu Kōenkai*

Maezurishū ["Proceedings of the Annual Congress of the Society of Automotive Engineers of Japan"] (2002), Vol. 22, No. 02, pp. 5–8

Non-Patent Reference Document 3: *Kinzoku* ["Metal" magazine] Vol. 74 (2004), No. 5, pp. 449–453

5   Non-Patent Reference Document 4: *Nippon Seramikkusu Kyōkai Gakujutsu Ronbunshi* (Journal of the Ceramic Society of Japan) (2003), Vol. 111, No. 129, pp. 852–856

Problems to be Overcome by the Invention

10   An object of the present invention is to provide a highly active and highly durable catalyst able to burn the particulate matter (PM) in diesel engine exhaust at low temperature. The catalyst does not contain noble metals and is thus inexpensive, and also its constituent materials are not volatized at exhaust gas temperatures, so it has superior durability. Another object is to provide a diesel particulate filter (DPF) for control of diesel

15   engine exhaust emissions that uses the catalyst.

Disclosure of the Invention

The foregoing objects are accomplished by means of a diesel engine exhaust gas particulate matter oxidation catalyst using a perovskite-type composite oxide that has

20   an NO adsorption domain over the entire range of 200–450°C, or at least a part thereof. This perovskite-type composite oxide may be represented by the structural formula RTO_3, wherein R is one or more elements selected from a group made up of the rare-earth elements, alkali metal elements excluding Na and alkaline-earth metal elements; and T is one or more elements selected from a group made up of the transition metal elements and

25   Mg, Al and Si. In particular, a preferable constitution is one wherein R comprises one or

more elements selected from a group made up of La, Sr, Ba, Ca and Li, and T comprises one or more elements selected from a group made up of Mn, Fe, Co, Cu, Zn, Ga, Zr, Mo, Mg, Al and Si. Note that Y is treated as a rare-earth element.

5   In an exhaust gas atmosphere that contains NO, this catalyst initiates the combustion of particulate matter constituted primarily of carbon in diesel engine exhaust at a temperature below 450°C. In addition, the present invention also provides a particulate matter filter for control of diesel engine exhaust emissions that carries any of these catalysts.

10   A diesel engine exhaust particulate matter (PM) oxidation catalyst that uses the perovskite-type composite oxide defined in the present invention is able to burn particulate matter that accumulates in a diesel particulate filter (DPF) for control of diesel engine exhaust emissions at low temperature, so the amount of particulate matter released into the atmosphere is reduced and also the temperature of the exhaust gas passing through the filter can be lowered in comparison with that in the prior art, and thus the load on

15 various members of the exhaust system is lessened. In addition, catalytic action with high activity can be achieved without containing noble metals, so the materials cost for the particulate filter can be reduced. Moreover, the catalyst according to the present invention does not contain material that is volatilized at exhaust gas temperatures, so it also has superior durability. Accordingly, the present invention improves the durability of a DPF

20 system and provides a greatly reduced total cost.

Brief Description of the Drawings

     FIG. 1 is a diagram showing the x-ray diffraction pattern of a perovskite-type composite oxide used in Working Example 1.

25   FIG. 2 is a graph of the changes in the NO concentration and CO_2

concentration in the output-side gas as a function of temperature in the warm-up process when simulated diesel engine exhaust is passed through a sample of particles of the perovskite-type composite oxide according to Working Example 1.

FIG. 3 is a graph of the change in the CO_2 concentration in the output-side gas as a function of temperature in the warm-up process when simulated diesel engine exhaust is passed through samples of honeycomb filters carrying catalysts obtained by means of Working Examples 1 and 2 and Comparative Example 1.

FIG. 4 is a graph of the change in the CO_2 concentration in the output-side gas as a function of temperature in the warm-up process when simulated diesel engine exhaust is passed through samples of honeycomb filters carrying catalysts obtained by means of Working Examples 2 and 3 and Comparative Example 1.

Preferred Embodiments of the Invention

In a conventional catalytic-type particulate filter, the nitrogen mono-oxide (NO) contained in diesel engine exhaust is oxidized on the surface of a metal catalyst such as Pt to form nitrogen dioxide (NO_2), and this NO_2 is used to oxidize (burn) particulate matter constituted primarily of carbon, thereby regenerating the filter.

In contrast, with the present invention, a perovskite-type composite oxide that has an NO adsorption domain at a temperature range below 450°C (e.g., 200–450°C) is used instead of the metal catalyst such as Pt. According to research conducted by the present inventors, this type of perovskite-type composite oxide was found to have the property of simultaneously inducing the reaction of oxidizing (burning) carbon particles to CO_2 and re-releasing NO at around 300–450°C. The particulate matter (PM) constituted primarily of carbon contained in diesel engine gas normally has a combustion temperature of 500°C or higher, so the perovskite-type composite oxide used in the present invention

has the catalytic action of burning PM at low temperature.

This perovskite-type composite oxide may be represented by the generic formula RTO_3. Here, R is one or more elements selected from a group made up of the rare-earth elements (Y is also treated as a rare-earth element), alkali metal elements excluding Na and alkaline-earth metal elements. However, it preferably contains at least one or more alkali metal elements and alkaline-earth metal elements. The above catalytic action is exhibited particularly markedly by such compositions. T is one or more elements selected from a group made up of the transition metal elements plus Mg, Al and Si. While there are no particular limitations on the rare-earth elements comprising R, they may be Y, La, Ce, Nd, Sm, Pr or the like, or preferably La. While there are no particular limitations on the transition-metal elements constituting T, they may be Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Zr, Mo, Ru, Rh, Pd, Ag, In, Sn, Pt, Au or the like, or preferably Ti, Mn, Fe, Co, Ni, Cu, Zn, Ga, Zr or Mo. Examples of elements other than the rare-earth elements that may constitute R include alkali metal elements excluding Na and alkaline-earth metal elements that may be contained in a form replacing a portion of the rare-earth elements. Examples include Li, K, Ca, Sr, Ba and the like, but these are preferably Li, Sr or Ba. From a standpoint of achieving a marked catalytic effect, rather than having R comprise only rare-earth elements, it is more preferable for it to include at least one or more of Li, Ca, Sr or Ba.

Patent Reference Document 3 discloses the use of a Na-based precipitating agent in order to obtain a precipitate of the composite oxide, but according to the research conducted by the present inventors, it is necessary for effecting the catalytic action for burning PM at low temperature to make the amount of Na within the perovskite-type composite oxide as small as possible, or specifically the Na content should be 0.7 mass % or less, or more preferably zero. It is typically difficult to remove Na-based constituents

that are incorporated from the raw materials. It was found that if Na-based constituents are present as impurities, the ignition temperature tends to increase as shown in the subsequent Working Examples.

5   In the perovskite-type composite oxide having such a composition, what has an NO adsorption domain within the temperature range 200–450°C, and has the property of simultaneously inducing the reaction of oxidizing (burning) carbon particles to CO_2 and re-releasing NO at around 300–450°C are realized. If a powder of such a perovskite-type composite oxide is carried upon a cordierite or SiC or other substrate constituting a honeycomb instead of the conventional Pt catalyst or the like, then one obtains a highly 10   active and highly durable diesel particulate filter (DPF) for purification of diesel engine exhaust emissions that is able to burn the particulate matter (PM) in diesel engine exhaust at low temperature.

The perovskite-type composite oxide used in the present invention may be produced by a coprecipitation method, organic complex method, alkoxide method, or a 15   method using an amorphous precursor, for example. Here follows a description of the various production methods.

Coprecipitation Method

In the coprecipitation method, an aqueous solution of salts of raw materials 20   that contains salts of the aforementioned elements in stoichiometric ratios appropriate to produce the perovskite-type composite oxide RTO_3 is prepared, this aqueous solution is mixed with a neutralizing agent to induce coprecipitation and then the coprecipitate thus obtained is dried and then heat-treated. The salts of the elements used are not particularly limited, but rather any of their sulfates, nitrates, phosphates, chlorides or other inorganic 25   salts, acetates, oxalates or other organic salts or the like may be used. Among these, the

acetates and nitrates are particularly suitable. The aqueous solution of salts of raw materials may be prepared by adding the salts of the aforementioned elements to water so as to reach the desired stoichiometric ratios and then stirring.

Then, this aqueous solution of salts of raw materials is mixed with a neutralizing agent to induce coprecipitation. There is no particular limitation with respect to the neutralizing agent used, but rather ammonia, potassium hydroxide and other inorganic bases, or triethylamine, pyridine or other organic bases can be used. In addition, the neutralizing agent is mixed in until the pH of the slurry formed after adding the neutralizing agent becomes 6–14. When mixed in this manner, a highly crystalline coprecipitate of hydroxides of the various elements can be obtained. The use of a base that contains Na at this time is not preferable because Na will become incorporated into the product.

If necessary, the coprecipitate thus obtained is rinsed with water and may be dried by vacuum drying or forced-air drying, for example, and then subjected to heat treatment at 600–1200°C, or preferably 800–1000°C to obtain the desired perovskite-type composite oxide. There is no particular limitation on the atmosphere used at the time of heat treatment as long as it is within a range wherein the perovskite-type composite oxide is produced, and an air, nitrogen, argon or hydrogen atmosphere or one of these combined with water vapor, or preferably an air or nitrogen atmosphere or one of these combined with water vapor may be used.

Organic Complex Method

In the organic complex method, a salt that forms an organic complex of citric acid, malic acid or the like and salts of the aforementioned elements may be added to water in the desired stoichiometric ratios and stirred to prepare an aqueous solution of salts of raw materials.

This aqueous solution of salts of raw materials is dried to form an organic complex of the aforementioned elements and then calcined and subjected to heat treatment ' to obtain the perovskite-type composite oxide.

The salts of the elements used may be the same as those used in the case of the coprecipitation method. The aqueous solution of salts of raw materials may also be prepared by dissolving a mixture of the raw material salts of the various elements in the desired stoichiometric ratios and then mixing this with an aqueous solution of a salt that forms an organic complex. Note that the molar ratio of the salt that forms an organic complex that is mixed in the blend is preferably around 1.2–3 mol per 1 mol of the perovskite-type composite oxide thus obtained.

Thereafter, this raw-material liquid is dried to obtain the aforementioned organic complex. There are no particular limitations to the drying conditions used as long as the temperature is such that the organic complex does not decompose, so for example, drying can be performed at room temperature to roughly 150°C, or preferably from room temperature to 110°C to quickly remove the moisture. The aforementioned organic complex is thus obtained.

The organic complex thus obtained is calcined and then heat-treated. Calcining may be performed by heating to 250°C or higher in a vacuum or in an inert gas atmosphere, for example. Thereafter, heat treatment at 600–1000°C, or preferably 600–950°C, for example may be performed to obtain the desired perovskite-type composite oxide. At this time, there is no particular limitation on the atmosphere used at the time of heat treatment as long as it is within a range wherein the perovskite-type composite oxide is produced, and an air, nitrogen, argon or hydrogen atmosphere or one of these combined with water vapor, or preferably an air or nitrogen atmosphere or one of these combined with water vapor may be used.

Alkoxide Method

In the alkoxide method, an alkoxide solution of raw materials that contains alkoxides of the aforementioned elements in stoichiometric ratios is prepared, this solution of raw materials is reacted with water to induce hydrolysis and obtain a precipitate. The precipitate thus obtained can be dried and then heat-treated to obtain the desired perovskite-type composite oxide.

The alkoxides of the elements used are not particularly limited as long as the elements mix uniformly, but rather for example, any alcoholates formed of methoxy, ethoxy, propoxy, isopropoxy, butoxy and other alkoxy groups may be used. The alkoxide solution of raw materials may be prepared by dissolving these alkoxides in an organic solvent so as to reach the desired stoichiometric ratios and then stirring and blending. The organic solvent that can be used is not particularly limited as long as it is able to dissolve the alkoxides of the elements, so for example, benzene, toluene, xylene and the like may be used.

Then, water is added to this raw material solution to induce hydrolysis and obtain a precipitate. If necessary, the precipitate thus obtained is rinsed with water and may be dried by vacuum drying or forced-air drying, for example, and then subjected to heat treatment at 500–1000°C, or preferably 500–850°C to obtain the desired perovskite-type composite oxide. There is no particular limitation on the atmosphere used at the time of heat treatment as long as it is within a range wherein the perovskite-type composite oxide is produced, and an air, nitrogen, argon or hydrogen atmosphere or one of these combined with water vapor, or preferably an air or nitrogen atmosphere or one of these combined with water vapor may be used.

Method using an Amorphous Precursor

In the method using an amorphous precursor, as disclosed by the present inventors in Japanese Patent Application No. 2004-61882 (and the corresponding United States Patent Application Serial No. 10/803,963 and European Patent Application No.

5   04007386.8) and Japanese Patent Application No. 2004-61901 (and the corresponding United States Patent Application Serial No. 10/809,709 and European Patent Application No. 04007387.6), a precursor substance comprising of a powdery amorphous containing the aforementioned elements in stoichiometric ratios appropriate to produce the perovskite-type composite oxide with the RTO_3 structure may be heat treated at low temperature to obtain

10   the perovskite-type composite oxide.

Such an amorphous precursor can be obtained by preparing an aqueous solution of salts of raw materials that contains salts of the aforementioned elements in stoichiometric ratios appropriate to produce the perovskite-type composite oxide with the RTO_3 structure, reacting this aqueous solution with a precipitating agent which is a

15   carbonate containing ammonium ion or an alkaline carbonate at a reaction temperature of 60°C or lower and at a pH of 6 or higher to make a precipitation product, and drying its filtrate.

More specifically, first a nitrate, sulfate, chloride or other aqueous mineral salt of R and a nitrate, sulfate, chloride or other aqueous mineral salt of T are dissolved in

20   water to prepare an aqueous solution wherein the molar ratio of the R element to the T element becomes 1:1. The molar ratio of the R element to the T element should ideally be made 1:1, but even if it is not 1:1 a perovskite-type composite oxide can still be formed. Accordingly, even if the molar ratio of the R element to the T element is shifted somewhat from 1:1, it is fine as long as it is a value that allows a perovskite-type composite oxide to

25   be formed. Note that the R element may comprise two or more components and the T

element may also comprise two or more components. In this case, the various components should be dissolved such that the molar ratio of the total number of moles of the elements that constitute R to the total number of moles of the elements that constitute T becomes roughly 1:1.

5   The ion concentrations of R and T in the solution in which the precipitate is to be formed are such that the upper limit is determined by the solubility of the salts used and should be such that crystalline compounds of R or T do not precipitate, but normally the total ion concentration of R and T is preferably roughly in the range 0.01–0.60 mol/L.

In order to obtain amorphous precipitates from this solution, it is preferable 10   to use a precipitating agent which is a carbonate containing ammonium ion or an alkaline carbonate, and examples of such a precipitating agent include ammonium carbonate, ammonium hydrogen carbonate and the like, but if necessary, aqua ammonia or another base may also be added. In addition, after a precipitate is formed using aqua ammonia or the like, it is also possible to blow in carbon dioxide to obtain an amorphous substance 15   suitable as the amorphous precursor to the perovskite-type composite oxide used in the present invention. When the amorphous precipitate is to be obtained, it is preferable that the pH of the solution be controlled to be in the range 6–11. If the pH is lower than 6, this is inappropriate because the rare-earth elements constituting R may not form a precipitate. On the other hand, if the pH is higher than 11, in the case of the use of a precipitating agent 20   alone, hydroxides or other crystalline precipitates may be formed without the precipitates thus formed being adequately converted to the amorphous state. In addition, the reaction temperature can be 60°C or lower. If the reaction is started at a temperature above 60°C, crystalline compound particles of R or T may be produced, and these may interfere with the conversion to an amorphous precursor and are thus not preferable. The use of a 25   precipitating agent that contains sodium was found to increase the ignition temperature.

This is thought to be because, if sodium is incorporated into the precursor, no matter how well it is washed, it will still remain at a concentration of roughly several hundred ppm and this will cause deleterious effects on the characteristics of ignition temperature and the like.

5   The amorphous precursor thus obtained is rinsed with water as optionally and may be dried by vacuum drying or forced-air drying, for example, and then subjected to heat treatment at 500–1000°C, or preferably 500–800°C to obtain the desired perovskite-type composite oxide. There is no particular limitation on the atmosphere used at the time of heat treatment as long as it is within a range wherein the perovskite-type composite oxide is produced, and an air, nitrogen, argon or hydrogen atmosphere or one of

10   these combined with water vapor, or preferably an air or nitrogen atmosphere or one of these combined with water vapor may be used.

Working Examples

Working Example 1

15   Lanthanum nitrate, strontium nitrate and manganese nitrate were mixed such that the molar ratios of the elements lanthanum, strontium and manganese became 0.8:0.2:1.0. This mixture was added to water in such amount that the total molar concentration of the elements lanthanum, strontium and manganese in the solution became 0.2 mol/L. This solution of raw materials was stirred while the temperature of the solution

20   was adjusted to 25°C, and at the stage that the temperature reached 25°C, a mixed solution of ammonia carbonate and aqua ammonia was added as a precipitating agent while adjusting to pH=9. Thereafter, stirring was continued for six hours while maintaining the reaction temperature at 25°C, allowing the production of the precipitate to advance sufficiently. The precipitate thus obtained was recovered by filtration, rinsed with water and

25   dried at 110°C. The powder thus obtained is called the precursor powder.

Next, this precursor powder was subjected to heat treatment at 600°C in air and thus calcined. FIG. 1 shows the x-ray diffraction pattern of the calcine thus obtained. Upon comparing the x-ray diffraction chart of FIG. 1 against a JCPDS card chart, this calcine was confirmed to be a substance with a $(La_{0.8}Sr_{0.2})MnO_3$ perovskite-type composite

5   oxide phase.

Working Example 2

Working Example 1 was repeated except that lanthanum nitrate, strontium nitrate and iron nitrate were used as the raw materials and were mixed such that the molar

10   ratios of the elements lanthanum, strontium and iron became 0.8:0.2:1.0.

As a result of analysis of the crystal structure by x-ray diffraction, the calcine was confirmed to have a $(La_{0.8}Sr_{0.2})FeO_3$ perovskite-type composite oxide phase. In addition, as a result of analysis of the composition by atomic absorption analysis, Na exhibited a value less than 1 ppm (less than the measurement limit).

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Working Example 3

A portion of the perovskite-type composite oxide obtained in Working Example 2 was sampled and subjected to heat treatment for 24 hours at 800°C. The heat treatment was performed in air.

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Comparative Example 1

Commercial SiO_2 (Wakogel C-100 made by Wako Pure Chemical Industries, Ltd.) was impregnated with Pt using an aqueous solution of $[Pt(NH_3)_4](OH)_2$ and dried by forced air for 12 hours at 120°C. The impregnate thus obtained was reduced for 4 hours at

25   400°C in 4% H_2 (the remainder being N_2) and then subsequently oxidized for 2 hours at

500°C in air to obtain SiO_2 containing Pt. The Pt content of the SiO_2 was 1 mass % at this time.

Comparative Example 2

Working Example 2 was repeated except that sodium hydroxide was used as the precipitating agent. As a result of atomic absorption analysis of the composition of the perovskite-type composite oxide particulate powder thus obtained, its Na content was found to be 0.77 mass %.

Evaluation of the PM Combustion Temperature Based on Particulate Samples

The PM combustion temperature was evaluated as follows in accordance with the method recited in *Kankyō Hozen Kenkyū Seikashū* ("Environmental Protection Research Results," National Institute of Industrial Health of Japan) (1999), 1, pp. 37-1–37-13.

Each of the powders obtained in Working Example 1 and Comparative Example 1 was press-formed with a die press at 500 kg/cm^2 and then crushed to prepare particulate samples with a grain size of 0.25–0.50 mm. As simulated PM, commercial carbon black was added to these particulate samples so as to become 1 mass.%, and they were mixed by shaking in a glass bottle. The state of contact between the carbon and the catalyst samples achieved by this mixing method becomes the state of "loose contact" close to that when PM is actually caught on a filter.

The aforementioned particulate samples mixed with carbon black were loaded into ventilated fixed beds which were put into contact with a constant flow of the simulated diesel engine exhaust gas shown in Table 1, so that the concentrations of CO_2 and NO in the gas passing through the ventilated fixed beds could be continuously measured. Then, once the flow of simulated diesel exhaust gas was started, the temperature was raised

from room temperature to 800°C at a warm-up rate of 10°C/minute while the concentrations of CO_2 and NO in the gas passing through the ventilated fixed beds was monitored.

The CO_2 concentration and the NO concentration were measured using a
5   Nicolet Nexus 470 FT-IR.

FIG. 2 illustrates an example of the changes in the CO_2 concentration and NO concentration in the case of Working Example 1. As one can see from FIG. 2, the downstream NO concentration dropped rapidly at 200–250°C and exhibited values below 200 ppm over approximately the range 250–350°C. This means that the NO drawn into the
10   air flow began to be adsorbed to the perovskite-type composite oxide at 200–250°C. Thereafter, as the CO_2 concentration increased rapidly from around 350°C, the NO concentration began to increase again. Then, from around 400°C, the NO concentration began to exhibit a value nearly equal to the inflow concentration of 500 ppm. Because the increase in the NO concentration from around 350°C occurred at the same time as the
15   increase in the CO_2 concentration accompanying the combustion of carbon black (simulated PM), clearly the NO adsorbed to the perovskite-type composite oxide was active in the combustion of carbon black. It is thought that when the NO adsorbed to the perovskite-type composite oxide is desorbed, some substance that has a strong oxidation activity (e.g., activated oxygen) is released, thus causing the combustion (oxidation) of carbon black. The
20   ignition temperature of the carbon black used here is around 560°C, so one can see that the perovskite-type composite oxide acted as a catalyst in inducing low-temperature combustion of the simulated PM.

The ignition temperature T_{10} was found in the measure as the temperature at which the amount of CO_2 generated as found by measuring the gas passing through the
25   ventilated fixed bed reached 10% of the total amount of CO_2 generated. The results in

Working Example 1 and Comparative Example 1 are presented in Table 2.

Table 1

NO	O_2	H_2O	N_2
500 ppm	10%	7%	Remainder

Table 2

	Composition	Ignition temperature (T_{10})
Working Example 1	$(La_{0.8}Sr_{0.2})MnO_3$	394°C
Comparative Example 1	Pt/SiO_2	430°C

As one can see from Table 2, despite containing no precious metal at all, the

5   perovskite-type composite oxide according to Working Example 1 demonstrated a lower

PM combustion temperature and higher activity than the Pt-impregnated SiO_2 catalyst

according to Comparative Example 1. In addition, this perovskite-type composite oxide

contains no water-soluble components such as potassium (K), so it can be expected to

exhibit good durability.

10   PM can be burned at low temperature using the perovskite-type composite

oxide that adsorbs NO in the 200–450°C temperature range, and thus the amount of PM

released can be reduced. The mechanism by which this low-temperature combustion of PM

occurs is unclear at the present time, but the following can be surmised.

[1]   NO within the exhaust gas is oxidized by O_2 in the atmosphere by

15   means of catalytic action of the perovskite-type composite oxide, thus being adsorbed to the

perovskite-type composite oxide in the form of NO_2 or nitrate ion.

[2]   When these species are again desorbed, a strongly oxidizing nitrogen

oxide or activated oxygen is formed.

[3]   The PM is caused to combust at low temperature by the nitrogen

20   oxide or activated oxygen thus formed, thereby producing NO and CO_2.

Evaluation of the PM Combustion Temperature Based on Honeycomb Filter Samples

Each of the powders obtained in Working Example 1, Working Example 2 and Comparative Example 1 was wash-coated onto a 200 cpsi cordierite honeycomb structure used as a DPF. The amount of coating was such that there were 10 parts by mass

5 powder to 100 parts by mass honeycomb structure. Thereafter, they were uniformly covered with commercial carbon black as simulated PM. The amount of carbon applied was such that there were 2 parts by mass powder to 100 parts by mass honeycomb structure.

The honeycomb filter samples thus obtained were loaded into ventilated fixed beds which were put into contact with a constant flow of the simulated diesel engine

10 exhaust gas shown in Table 3, so that the concentrations of CO_2 in the gas passing through the ventilated fixed beds could be continuously measured. In Table 3, SV is the spatial velocity represented by the following equation.

$$SV = \frac{\text{total gas flow (liters/minute)}}{\text{catalyst volume (cc)}}$$

Then, once the flow of simulated diesel vehicle exhaust gas was started, the

15 temperature was raised from room temperature to 750°C at a warm-up rate of 10°C/minute while the CO_2 concentration in the gas passing through the ventilated fixed beds was monitored.

The CO_2 concentration was measured using a Shimadzu FID-methanizer.

FIG. 3 illustrates an example of the changes in the CO_2 concentration in

20 Working Examples 1 and 2 and Comparative Example 1. As one can see from FIG. 3, the increase in the CO_2 concentration accompanying carbon black (simulated PM) combustion in Working Examples 1 and 2 occurred starting at a low temperature of approximately 300°C. In other words, in the same manner as in the particulate samples above, one can see that the perovskite-type composite oxide acted as a catalyst in inducing low-temperature

combustion of the simulated PM.

The ignition temperature T_{10} is presented in Table 4.

Table 3

NO	O_2	H_2O	N_2	SV
1000 ppm	10%	7%	Remainder	20000/h

Table 4

	Composition	Ignition temperature (T_{10})
Working Example 1	$(La_{0.8}Sr_{0.2})MnO_3$	397°C
Working Example 2	$(La_{0.8}Sr_{0.2})FeO_3$	402°C
Comparative Example 1	Pt/SiO_2	478°C

5   As one can see from Table 4, despite containing no precious metal at all, the perovskite-type composite oxide catalysts according to the present invention (Working Examples 1 and 2) were confirmed to exhibit the action of markedly lowering the PM combustion temperature, and were found to have a high practical value. In other words, the catalyst according to the present invention can be expected to give higher performance and

10   higher reliability than the conventional precious-metal catalysts in practice.

Evaluation of Catalytic Effectiveness after Heating to High Temperature

        The perovskite-type composite oxide obtained after heat treatment (after heat treatment at 800°C for 24 hours) in Working Example 3 was evaluated in the same

15   manner as in FIG. 3 above and the results are shown in FIG. 4. For comparison, FIG. 4 also illustrates the results with a Pt catalyst that was not heat-treated (that of Comparative Example 1) and a perovskite-type composite oxide that was not subjected to heat treatment (that of Working Example 2), for comparison with that of Working Example 3.

        As is clear from the results of FIG. 4, in comparison with that of the

20   unheated Working Example 2, the oxide of Working Example 3 that was subjected to heat

treatment exhibited a somewhat lower efficiency of conversion from carbon to CO_2 in the low-temperature region, but no extreme drop in activity occurred. Moreover, that of Working Example 3 that was subjected to heat treatment kept activity superior to that of the conventional Pt catalyst according to Comparative Example 1 that underwent catalytic evaluation without being subjected to heat treatment. In other words, the perovskite-type composite oxide according to the present invention keeps its catalytic activity even under severe environments and is able to perform the combustion of particulate matter in an environment at a lower temperature in comparison to conventional catalysts.

Note that when the ignition temperature for Working Example 2 and Comparative Example 2 were compared, that of Working Example 2 was 358°C while that of Comparative Example 2 was 380°C, thus confirming that ones that contain sodium have a slightly higher ignition temperature.